1,7-Asymmetric Induction in a Nitrogen Ring Expansion Process Facilitated by in situ Tethering

Kelly Furness and Jeffrey Aubé*

Supporting Information

Details of X-ray crystallographic determination of 3c.

A. Crystal Data

Empirical Formula	$O_2NC_{19}H_{29}$
Formula Weight	303.44
Crystal Color, Habit	Clear, Prism
Crystal Dimensions	0.30 X 0.45 X 0.05 mm
Crystal System	monoclinic
Lattice Type	Primitive
No. of Reflections Used for Unit Cell Determination (2q range)	14 (35.0 - 43.8^o)
Omega Scan Peak Width at Half-height	0.90^o
Lattice Parameters	a = 11.265(6) Å b = 6.576(6) Å c = 12.408(4) Å b = 99.9795 Å V = 905.2(8) Å^3
Space Group	$P2_1$ (#4)
Z value	2
D_{calc}	1.113 g/cm^3
F_{000}	332.00
m(CuKa)	5.55 cm^{-1}

B. Intensity Measurements

Diffractometer	Rigaku AFC5R
Radiation	CuKa (l = 1.54178 Å) graphite monochromated
Attenuator	Ni foil (factors = 1.00, 3.81, 13.15, 49.56)
Take-off Angle	6.0°
Detector Aperture	6.0 mm horizontal 6.0 mm vertical
Crystal to Detector Distance	400 mm
Voltage, Current	50kV, 150mA
Temperature	23.0°C
Scan Type	w-2q
Scan Rate	16.0°/min (in w) (up to 3 scans)
Scan Width	(1.78 + 0.30 tan q)°
$2q_{max}$	120.3°
No. of Reflections Measured	Total: 3154
Corrections	Unique: 1493 (R_{int} = 0.033) Lorentz-polarization Absorption (trans. factors: 0.7934 - 0.9975)

C. Structure Solution and Refinement

Structure Solution	Direct Methods (SIR92)
Refinement	Full-matrix least-squares on F
Function Minimized	S w $(\|Fo\| - \|Fc\|)^2$

Least Squares Weights	$1/s^2(Fo) = 4Fo^2/s^2(Fo^2)$
p-factor	0.0300
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (I>3.00s(I))	980
No. Variables	198
Reflection/Parameter Ratio	4.95
Residuals: R; Rw	0.060 ; 0.065
Goodness of Fit Indicator	2.18
Max Shift/Error in Final Cycle	0.14
Maximum peak in Final Diff. Map	0.21 $e^-/Å^3$
Minimum peak in Final Diff. Map	-0.19 $e^-/Å^3$

Table 1. Atomic coordinates and B_{iso}/B_{eq}

atom	x	y	z	B_{eq}
O(1)	-0.0889(3)	0.0364	-0.3852(3)	6.5(1)
O(2)	-0.2706(2)	-0.7383(8)	-0.5125(2)	4.57(8)
N(1)	-0.0336(3)	-0.2925(9)	-0.3606(3)	4.1(1)
C(1)	-0.0126(4)	-0.094(1)	-0.3503(4)	4.1(1)
C(2)	0.1102(4)	-0.0315(9)	-0.2874(4)	4.5(1)
C(3)	0.1338(4)	-0.087(1)	-0.1676(4)	4.4(1)
C(4)	0.1851(4)	-0.302(1)	-0.1448(4)	4.0(1)
C(5)	0.0920(4)	-0.459(1)	-0.1987(4)	4.8(1)
C(6)	0.0596(4)	-0.4445(9)	-0.3200(4)	4.2(1)
C(7)	-0.1437(4)	-0.370(1)	-0.4305(4)	4.8(1)
C(8)	-0.2251(4)	-0.4896(9)	-0.3669(3)	4.1(1)
C(9)	-0.3227(4)	-0.605(1)	-0.4438(4)	3.8(1)
C(10)	-0.4107(4)	-0.709(1)	-0.3842(3)	3.8(1)
C(11)	-0.3907(4)	-0.902(1)	-0.3434(4)	4.5(1)
C(12)	-0.4697(5)	-0.999(1)	-0.2858(4)	5.5(1)
C(13)	-0.5702(5)	-0.890(1)	-0.2673(5)	6.8(2)
C(14)	-0.5936(5)	-0.698(1)	-0.3073(5)	6.6(2)
C(15)	-0.5128(4)	-0.604(1)	-0.3660(4)	4.9(1)
C(16)	0.2349(5)	-0.344(1)	-0.0216(4)	5.3(1)
C(17)	0.3370(6)	-0.196(1)	0.0187(5)	8.6(2)

Table 1. Atomic coordinates and B_{iso}/B_{eq} (continued)

atom	x	y	z	B_{eq}
C(18)	0.1395(6)	-0.308(2)	0.0485(5)	10.1(2)
C(19)	0.2833(8)	-0.560(1)	-0.0085(6)	11.2(3)
H(1)	0.1091	0.1021	-0.3091	13.165
H(2)	0.1685	-0.0992	-0.3266	9.947
H(3)	0.1985	0.0138	-0.1269	7.001
H(4)	0.0506	-0.0742	-0.1360	5.038
H(5)	0.2475	-0.2956	-0.1866	4.524
H(6)	0.1215	-0.5791	-0.1745	5.465
H(7)	0.0244	-0.4826	-0.1628	10.330
H(8)	0.0382	-0.5395	-0.3595	9.570
H(9)	0.1413	-0.4052	-0.3522	7.562
H(10)	-0.1827	-0.2732	-0.4716	8.191
H(11)	-0.1185	-0.4323	-0.4978	6.735
H(12)	-0.2593	-0.3922	-0.3036	4.830
H(13)	-0.1751	-0.5838	-0.3200	5.280
H(14)	-0.3718	-0.5179	-0.4998	3.231
H(15)	-0.2243	-0.7956	-0.4584	8.762
H(16)	-0.3232	-0.9778	-0.3521	7.152
H(17)	-0.4582	-1.1340	-0.2430	7.952
H(18)	-0.6251	-0.9580	-0.2232	6.375

Table 1. Atomic coordinates and B_{iso}/B_{eq} (continued)

atom	x	y	z	B_{eq}
H(19)	-0.6558	-0.6147	-0.2894	11.835
H(20)	-0.5241	-0.4432	-0.4036	10.735
H(21)	0.3551	-0.0884	0.0059	14.238
H(22)	0.3921	-0.2221	-0.0408	16.238
H(23)	0.3650	-0.2281	0.0965	9.389
H(24)	0.3314	-0.5807	-0.0415	17.399
H(25)	0.3131	-0.5890	0.0778	9.917
H(26)	0.1984	-0.6090	-0.0308	23.142
H(27)	0.1626	-0.3499	0.1204	7.398
H(28)	0.0692	-0.4102	0.0247	10.429
H(29)	0.1477	-0.1506	0.0513	15.238

$B_{eq} = 8/3\ p^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos g + 2U_{13}(aa^*cc^*)\cos b + 2U_{23}(bb^*cc^*)\cos a)$

Table 2. Anisotropic Displacement Parameters

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1)	0.059(2)	0.063(3)	0.116(3)	0.025(2)	-0.008(2)	0.007(2)
O(2)	0.047(2)	0.065(3)	0.059(2)	-0.006(2)	0.004(2)	-0.001(2)
N(1)	0.037(2)	0.042(3)	0.071(3)	-0.005(2)	-0.004(2)	-0.003(2)
C(1)	0.045(3)	0.048(4)	0.065(3)	0.003(3)	0.015(2)	0.004(3)
C(2)	0.050(3)	0.037(3)	0.076(4)	0.000(3)	-0.007(2)	-0.001(3)
C(3)	0.053(3)	0.046(3)	0.064(3)	-0.002(3)	-0.001(2)	-0.011(3)
C(4)	0.038(2)	0.048(3)	0.066(3)	0.001(3)	0.008(2)	0.002(3)
C(5)	0.074(3)	0.040(3)	0.065(4)	-0.000(3)	-0.002(3)	0.004(3)
C(6)	0.050(3)	0.036(3)	0.069(3)	0.001(3)	-0.006(2)	-0.014(3)
C(7)	0.054(3)	0.069(4)	0.054(3)	-0.021(3)	-0.005(2)	0.003(3)
C(8)	0.046(2)	0.055(3)	0.051(3)	-0.004(3)	-0.001(2)	0.002(3)
C(9)	0.040(3)	0.050(3)	0.053(3)	0.008(3)	0.004(2)	-0.002(3)
C(10)	0.035(3)	0.057(3)	0.049(3)	-0.001(3)	-0.004(2)	-0.008(3)
C(11)	0.047(3)	0.060(4)	0.062(3)	0.004(3)	0.002(3)	0.007(3)
C(12)	0.076(4)	0.072(4)	0.057(3)	-0.028(4)	0.006(3)	0.009(3)
C(13)	0.056(4)	0.120(7)	0.084(4)	-0.032(4)	0.012(3)	-0.012(4)
C(14)	0.048(3)	0.110(6)	0.093(5)	-0.000(4)	0.016(3)	-0.007(5)
C(15)	0.054(3)	0.068(4)	0.064(3)	0.003(3)	0.008(3)	-0.001(3)
C(16)	0.076(4)	0.062(4)	0.061(4)	-0.007(3)	0.005(3)	0.006(3)
C(17)	0.104(5)	0.099(5)	0.101(5)	-0.045(5)	-0.044(4)	0.017(4)

Table 2. Anisotropic Displacement Parameters (continued)

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(18)	0.140(5)	0.189(9)	0.053(4)	-0.038(7)	0.017(4)	0.017(5)
C(19)	0.200(9)	0.094(6)	0.101(6)	0.038(6)	-0.065(5)	0.012(5)

The general temperature factor expression:
$\exp(-2p^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl))$

Table 3. Bond Lengths(Å)

atom	atom	distance	atom	atom	distance
O(1)	C(1)	1.239(8)	O(2)	C(9)	1.419(8)
O(2)	H(15)	0.86	N(1)	C(1)	1.326(9)
N(1)	C(6)	1.473(9)	N(1)	C(7)	1.477(8)
C(1)	C(2)	1.524(9)	C(2)	C(3)	1.51(1)
C(2)	H(1)	0.92	C(2)	H(2)	0.99
C(3)	C(4)	1.532(9)	C(3)	H(3)	1.05
C(3)	H(4)	1.08	C(4)	C(5)	1.540(9)
C(4)	C(16)	1.559(9)	C(4)	H(5)	0.94
C(5)	C(6)	1.49(1)	C(5)	H(6)	0.89
C(5)	H(7)	0.96	C(6)	H(8)	0.81
C(6)	H(9)	1.10	C(7)	C(8)	1.53(1)
C(7)	H(10)	0.89	C(7)	H(11)	1.01
C(8)	C(9)	1.526(9)	C(8)	H(12)	1.13
C(8)	H(13)	0.96	C(9)	C(10)	1.500(9)
C(9)	H(14)	0.99	C(10)	C(11)	1.37(1)
C(10)	C(15)	1.394(9)	C(11)	C(12)	1.39(1)
C(11)	H(16)	0.93	C(12)	C(13)	1.39(1)
C(12)	H(17)	1.03	C(13)	C(14)	1.37(1)
C(13)	H(18)	1.00	C(14)	C(15)	1.40(1)
C(14)	H(19)	0.95	C(15)	H(20)	1.15

Table 3. Bond Lengths(Å) (continued)

atom	atom	distance	atom	atom	distance
C(16)	C(17)	1.52(1)	C(16)	C(18)	1.51(1)
C(16)	C(19)	1.52(1)	C(17)	H(21)	0.76
C(17)	H(22)	1.06	C(17)	H(23)	0.98
C(18)	H(27)	0.93	C(18)	H(28)	1.04
C(18)	H(29)	1.04	C(19)	H(24)	0.75
C(19)	H(25)	1.08	C(19)	H(26)	1.00

Table 4. Bond Angles(°)

atom	atom	atom	angle	atom	atom	atom	angle
C(9)	O(2)	H(15)	93.5	C(1)	N(1)	C(6)	122.0(6)
C(1)	N(1)	C(7)	121.0(6)	C(6)	N(1)	C(7)	116.2(6)
O(1)	C(1)	N(1)	123.2(7)	O(1)	C(1)	C(2)	120.2(7)
N(1)	C(1)	C(2)	116.5(7)	C(1)	C(2)	C(3)	115.4(6)
C(1)	C(2)	H(1)	98.3	C(1)	C(2)	H(2)	104.3
C(3)	C(2)	H(1)	120.8	C(3)	C(2)	H(2)	110.9
H(1)	C(2)	H(2)	105.3	C(2)	C(3)	C(4)	113.7(6)
C(2)	C(3)	H(3)	108.0	C(2)	C(3)	H(4)	108.8
C(4)	C(3)	H(3)	106.7	C(4)	C(3)	H(4)	109.2
H(3)	C(3)	H(4)	110.5	C(3)	C(4)	C(5)	109.4(5)
C(3)	C(4)	C(16)	113.9(6)	C(3)	C(4)	H(5)	98.7
C(5)	C(4)	C(16)	114.1(6)	C(5)	C(4)	H(5)	107.9
C(16)	C(4)	H(5)	111.7	C(4)	C(5)	C(6)	115.1(6)
C(4)	C(5)	H(6)	105.3	C(4)	C(5)	H(7)	116.3
C(6)	C(5)	H(6)	114.2	C(6)	C(5)	H(7)	113.8
H(6)	C(5)	H(7)	88.9	N(1)	C(6)	C(5)	115.1(6)
N(1)	C(6)	H(8)	101.4	N(1)	C(6)	H(9)	108.0
C(5)	C(6)	H(8)	124.2	C(5)	C(6)	H(9)	108.0
H(8)	C(6)	H(9)	98.1	N(1)	C(7)	C(8)	113.2(6)
N(1)	C(7)	H(10)	111.7	N(1)	C(7)	H(11)	107.3

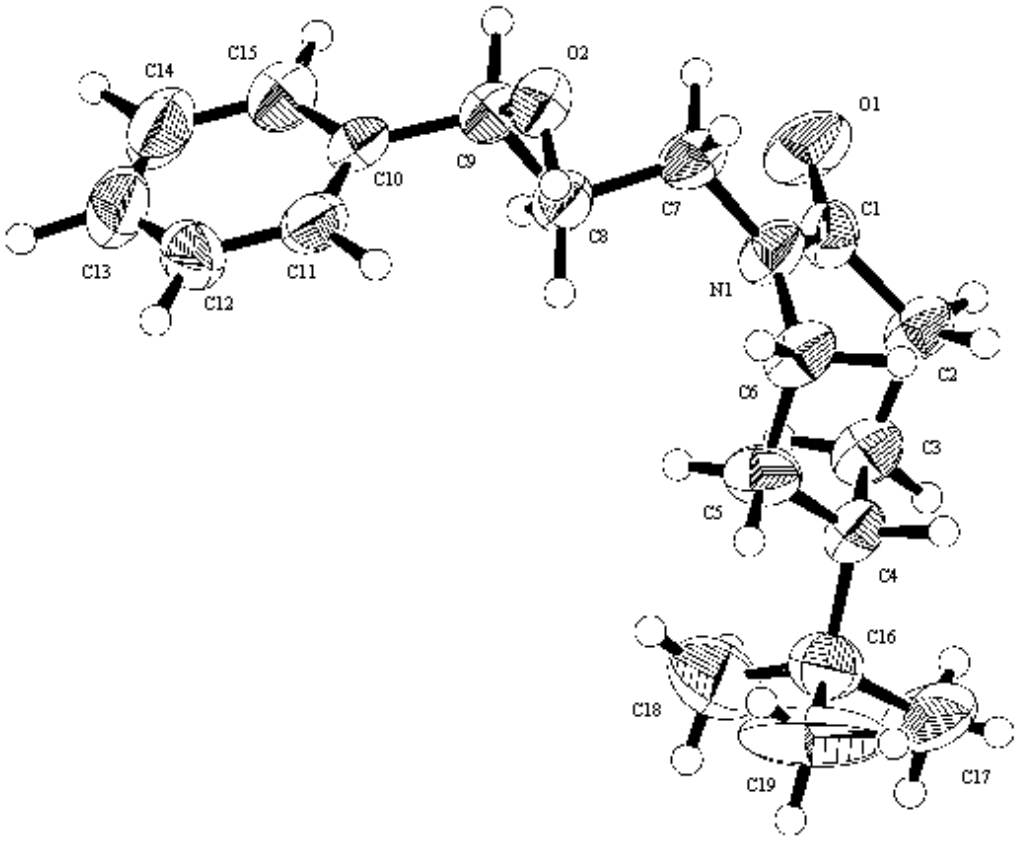
Table 4. Bond Angles(°) (continued)

atom	atom	atom	angle	atom	atom	atom	angle
C(8)	C(7)	H(10)	112.6	C(8)	C(7)	H(11)	120.0
H(10)	C(7)	H(11)	89.8	C(7)	C(8)	C(9)	111.3(5)
C(7)	C(8)	H(12)	112.1	C(7)	C(8)	H(13)	107.5
C(9)	C(8)	H(12)	114.9	C(9)	C(8)	H(13)	110.0
H(12)	C(8)	H(13)	100.3	O(2)	C(9)	C(8)	110.8(5)
O(2)	C(9)	C(10)	113.1(6)	O(2)	C(9)	H(14)	100.0
C(8)	C(9)	C(10)	112.6(6)	C(8)	C(9)	H(14)	114.0
C(10)	C(9)	H(14)	105.8	C(9)	C(10)	C(11)	121.6(7)
C(9)	C(10)	C(15)	119.3(7)	C(11)	C(10)	C(15)	119.1(7)
C(10)	C(11)	C(12)	122.4(7)	C(10)	C(11)	H(16)	122.7
C(12)	C(11)	H(16)	114.9	C(11)	C(12)	C(13)	117.5(8)
C(11)	C(12)	H(17)	128.7	C(13)	C(12)	H(17)	113.0
C(12)	C(13)	C(14)	121.7(9)	C(12)	C(13)	H(18)	117.3
C(14)	C(13)	H(18)	120.9	C(13)	C(14)	C(15)	119.7(9)
C(13)	C(14)	H(19)	123.6	C(15)	C(14)	H(19)	116.0
C(10)	C(15)	C(14)	119.5(8)	C(10)	C(15)	H(20)	115.1
C(14)	C(15)	H(20)	125.4	C(4)	C(16)	C(17)	109.3(6)
C(4)	C(16)	C(18)	111.4(6)	C(4)	C(16)	C(19)	109.4(7)
C(17)	C(16)	C(18)	106.3(8)	C(17)	C(16)	C(19)	109.0(8)
C(18)	C(16)	C(19)	111.3(9)	C(16)	C(17)	H(21)	137.7

Table 4. Bond Angles(°) (continued)

atom	atom	atom	angle	atom	atom	atom	angle
C(16)	C(17)	H(22)	99.7	C(16)	C(17)	H(23)	106.3
H(21)	C(17)	H(22)	78.1	H(21)	C(17)	H(23)	110.6
H(22)	C(17)	H(23)	121.5	C(16)	C(18)	H(27)	113.4
C(16)	C(18)	H(28)	108.4	C(16)	C(18)	H(29)	96.2
H(27)	C(18)	H(28)	98.7	H(27)	C(18)	H(29)	104.9
H(28)	C(18)	H(29)	135.4	C(16)	C(19)	H(24)	113.1
C(16)	C(19)	H(25)	108.3	C(16)	C(19)	H(26)	87.8
H(24)	C(19)	H(25)	112.4	H(24)	C(19)	H(26)	122.7
H(25)	C(19)	H(26)	109.6				

Crystal 282


C15
C14
O2
O1
C10
C9
C7
C1
C8
C13
C11
N1
C12
C2
C6
C3
C5
C4
C16
C18
C19
C17